Preparation and Properties of a Compound in the B–C–N System

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Boron–carbon–nitrogen powders were prepared by a chemical process based on simultaneous nitridation of boric acid and carbonization of saccharose in molten urea. From the chemical analysis and infrared spectroscopy of the products obtained by changing the ratio of the three starting materials to control the BN/C ratio, the balance composition, which was obtained with neither free carbon nor boron nitride coexistent, was found to correspond to the formula BC_4N. The powder had a turbostratic structure related rather to graphite than to boron nitride, based on its graphitization behavior. A sandwich structure model in which single boron nitride monolayers are inserted between pairs of carbon layers is proposed to interpret these facts and the infrared spectra, sharp contrast with a CVD product, which is considered as having B–N and C–C copolymer layer. © 1995 Academic Press, Inc.

1. INTRODUCTION

Graphite and hexagonal boron nitride are two structurally similar isoelectronic substances. The former has been known to mankind for many centuries, due to its natural occurrence, while the latter was synthesized as recently as the previous century (1) but has became a base of many important materials. Thus hybridizing these two constituents to form a ternary system has been attempted. Many reaction systems containing all three elements—boron, carbon, nitrogen—have been studied; however, synthesis of a ternary B–C–N compound has not been announced for a long time.

The boric oxide–carbon–nitrogen system, for example, was used to yield boron nitride or carbide by controlling reaction conditions. A thermodynamic model was established to describe the system, but the existence of such a ternary compound was not taken into account (2). This can be explained by the inability to prepare a B–C–N compound in such an experimental system, where carbon was present in elemental form (solid) and as a compound—boron carbide (solid) and carbon oxides (gas). Boron occurred exclusively in the form of a compound—

boric oxide and boron carbide. Nitrogen worked as a reactive component only to produce boron nitride (solid). As graphite, boron nitride, and boron carbide rank among the thermodynamically stable compounds in a neutral environment, any formation of an alloy is beyond expectation. This was experimentally proved by Badzian *et al.*, who could not synthesize a ternary compound by solid-state alloying the constituents at 2500°C and 30 kbar (3).

A hybrid B–C–N phase was first announced by Kosolapova *et al.*, who found such a phase in products obtained by nitriding an elemental mixture of boron with carbon (4). This means that there was a certain interaction between carbon and just-forming boron nitride to yield a B–C–N phase; however, boron nitride and unreacted carbon must be considered major components of the final products. From the above facts it can be deduced that another approach must be chosen to synthesize a ternary compound with distinctive character: carbonization and nitridation must occur simultaneously to yield a ternary B–C–N compound.

Reaction in the gaseous phase ensures such conditions and thus Badzian could declare synthesis of a graphite–boron nitride solution by chemical deposition from a gaseous mixture consisting of boron trichloride, tetrachloromethane, nitrogen, and hydrogen, optimally at 1900°C, as deposits prepared at lower temperature were contaminated by boron carbide (5).

Use of ammonia instead of nitrogen allowed lower temperature pyrolysis. Deposits obtained from boron trichloride, acetylene, and ammonia at 700°C had the approximate formula $B_{0.35}C_{0.30}N_{0.35}$ (6). Another improvement was reached when nitrogen and carbon were carried by common molecules so that the products showed better homogeneity. A substance having the formula BC_2N was prepared by Sasaki *et al.* (7) by pyrolysis of a boric trichloride with acetonitrile at 850°C. A deviation from equimolarity between boron and nitrogen was found by Moore *et al.* (8, 9), who prepared nitrogen-deficient solids by pyrolyzing various hydrocarbons (CH_4, C_3H_8, C_2H_2) with other gaseous sources. Materials obtained at 1500–1900°C had the composition $B_{0.29}C_{0.37}N_{0.30}$. Another, boron-rich phase, $B_{0.58}C_{0.25}N_{0.17}$, was synthesized

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from a BCl_3–NH_3–CH_4–H_2 mixture at 1377°C and 25 Torr (10). When an aliphatic borazon precursor was used, a nitrogen-rich, graphitic material was prepared with the formula $B_{0.28}C_{0.37}N_{0.35}$ (11). By repeating the procedure of Kaner et al. (6), Saugnac et al. (12) obtained a solid solution with carbon-rich domains of an ideal C_5B_2N composition.

All the ternary substances form turbostratic solids and the structure is derived from graphite rather than from boron nitride. The structural model is built by replacing two adjacent carbon atoms by a boron–nitrogen pair in a graphite monolayer, which can be shared by both contributors (C and BN) in any ratio. The presence of all three atoms in each monolayer has been suggested from electrospectroscopic measurements (5–7, 12). Calculations based on lattice energy and bond strength have been carried out to determine the arrangement of the elements. Three structural models, differing in electronic properties in being either semiconductor or semimetal (13, 14), were considered.

Taken from the point of view of borides, boron-rich solids containing singular nitrogen or carbon atoms are structurally based on polyhedrons of boron atoms and are synthesized at high temperatures as equilibrium phases (15, 16). In boron nitride, however, boron and nitrogen atoms are directly linked with each other in either graphite-like layers or diamond-like solids. A strong covalent bond results in difficult crystallization without the aid of an additive.

In this paper we present a new chemical method of preparing a ternary B–C–N compound and discuss some chemical and structural properties of the product in relation to the resemblance between carbon and boron nitride. The ternary compound is considered to be a noncrystalline quasi-equilibrium substance between two stable phases with terminal compositions of BN and C and to have structure and bonding similar to both. Crystallization of the substance (accelerated by some catalysts or fluxes, for example) is supposed to result in separation of the stable terminal phases.

2. EXPERIMENTAL

The principle of the method used here consists of high solubility of certain compounds in urea. O'Connor, for example, dissolved boric acid in urea to prepare turbostratic boron nitride (tBN) (17). Mang et al. dissolved urea in molten saccharose (18) and we dissolved saccharose in urea (19) to prepare nitrogen-containing turbostratic carbon (tC), where urea acted as a source of nitrogen as well as exerting a solvation effect.

To synthesize a B–C–N compound, boric acid and saccharose were dissolved in urea. One part of boric acid was mixed with 2.2 weight parts of urea and with various ratios of saccharose in a porcelain mortar. The mixture was heated in a Pyrex beaker at 130–150°C for 1 hr and then the temperature was raised to 220°C for an additional 2 hr. Pressure in the system was kept at 6–8 Torr to remove volatile exhausts. The reaction began with complete melting of the mixture. Then the melt gradually lost its transparency, turned to a brown viscous liquid, and later foamed; finally, solidification of the foam was observed.

After cooling, the obtained B–C–N precursor was pulverized in an agate ball mill and then annealed in nitrogen (1.5 cm/s) for the next 3 hr. Sintered alumina boats, quartz tubes, and a Kanthal furnaces were used for the temperature range 500–1200°C, and graphite crucibles and an RF induction furnace for higher temperatures (1300–2150°C).

Carbon was determined by an automatic analyzer RW-12, oxygen and nitrogen by TC 136, both from LECO, U.S.A. For phase analysis, XRD patterns (CuK_α, diffractometer PW 1130, Philips, Holland), infrared spectra (spectrometer FTS-65, Bio-Rad, Japan), and SEMs (Akashi DS 130, Japan) were employed.

3. EXPERIMENTAL RESULTS

3.1. Chemical Composition

The subject of this study consists of five elements—hydrogen, boron, carbon, nitrogen, and oxygen—as shown in Fig. 1. It was necessary to reduce the number of elements to three to envision the composition of analyzed samples. Hydrogen is the lightest element of the system and, additionally, it could be expected that its content in thermally treated samples was substantially lower than in starting mixtures, since water and ammonia release was observed in the first stage of the precursor preparation. Moreover, hydrogen is the only element of the system which is not directly bound to boron, as can be judged from the chemical character of the starting compounds. Boron can be regarded as a central atom of the system. It is the only element in this experimental system which does not form volatile compounds.
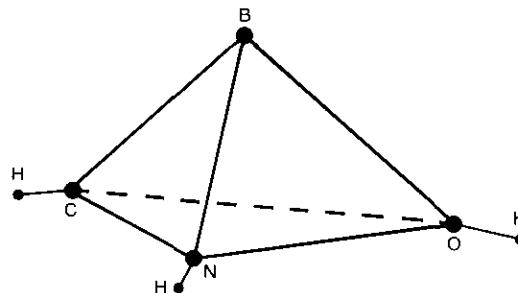

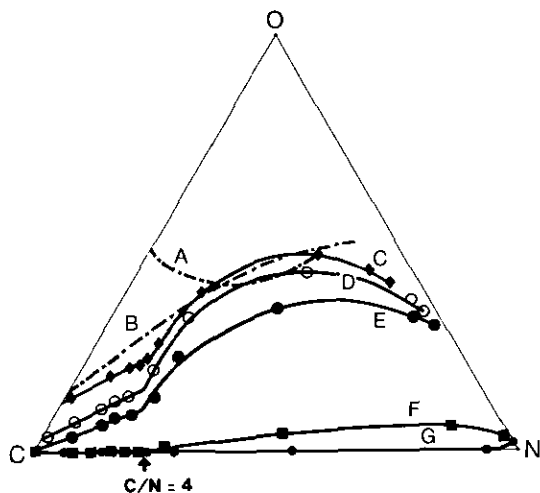FIG. 1. Binding facilities in the H–B–C–N–O system.

FIG. 2. C-N-O ternary diagram of samples prepared by heating boric acid-urea mixtures with varying saccharose addition: (A) 220°C, (B) 500°C, (C) 700°C, (D) 900°C, (E) 1100°C, (F) 1300°C, (G) 1500°C.

Concentrations of carbon, nitrogen, and oxygen have therefore been chosen to characterize the composition of analyzed specimens. The analytical data were normalized to 100% and plotted in a ternary diagram (Fig. 2). There is a set of lines in the diagram. Each line was drawn using C-N-O rational points representing the composition of a series obtained by varying the ratio of saccharose in the starting mixture. Line A is related to the series of precursors and the others (B-G) are related to those treated at marked temperatures. The lines can be classified into two groups according to their shapes. The first group contains two lines, A and B (precursors and 500°C), and the second group the rest—from lines C to G (from 700°C upward). The difference among the lines in the second group mainly consists in the positions of maxima related to samples with the highest oxygen content. The higher the temperature, the lower the content of oxygen, due to the reducing effect of carbon. Line F (1300° C) has almost a linear shape and this temperature was the lowest at which oxygen-free samples were prepared. Besides boron nitride prepared only from boric acid and urea, which always contains a certain amount of oxygen, all the samples annealed at 1500°C were oxygen-free within the entire range of examined compositions as the line has been confluent with the C-N side of the diagram (G). Additionally, in this series, the weight deficiency completing the results of elemental analysis to 100% was equimolar with nitrogen with a fluctuation less than ±2% in mass when ascribed to boron.

Lines C-G for temperatures 700°C and higher are composed of two parts joined at an inflection point. The parts adjacent to the nitrogen vertex of the diagram have a bow-like shape, while the other arms are rather linear, as

the samples tended to be enriched in carbon when the ratio of saccharose in the starting mixtures was increased.

3.2. Structural Analysis

XRD patterns of a series of B-C-N samples annealed at 1300°C are shown in Fig. 3. They had one broad peak corresponding to the (002) diffraction line and another characteristic peak related to the (10) line, thus reflecting the layered nature of the turbostratic boron nitride and carbon (tBN, tC). Pure contributors (tBN and tC) had larger and better-ordered crystallites than complex specimens, as the peaks were slimmer and their maxima shifted to higher 2θ angles. In the pattern of sample B, containing a rather low amount of carbon, formation of boron carbide at temperatures as low as 1300°C was noted.

Ordering of layered crystals was evaluated by the interlayer distance d_{002}. Dependence of this parameter on the BN/C ratio in the samples heated in 1300°C is shown
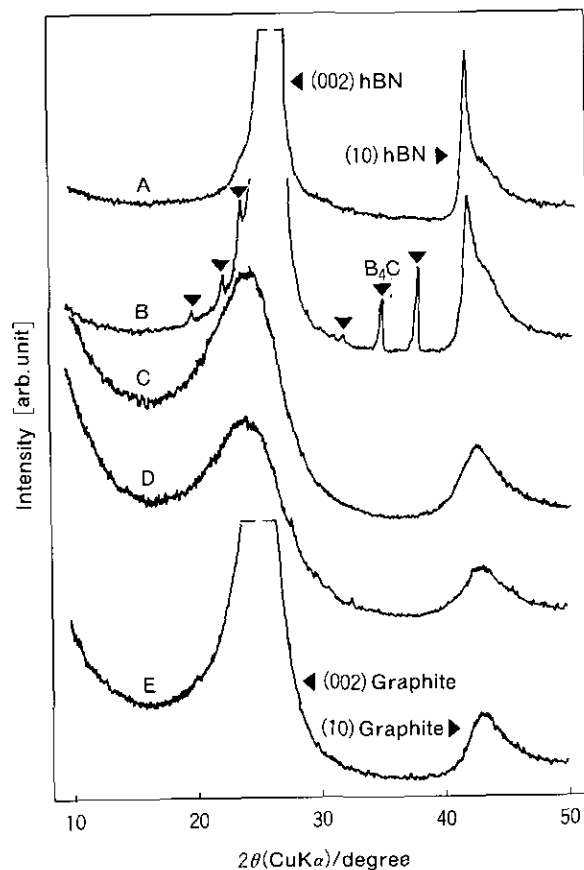

FIG. 3. XRD patterns of B-C-N powders obtained from urea-boric acid-saccharose mixtures with a changing saccharose ratio, prepared at 1300°C: (A) no saccharose addition, (B) 10% (C) 30%, (D) 60%, (E) saccharose-urea 1 : 1 mixture without boric acid.
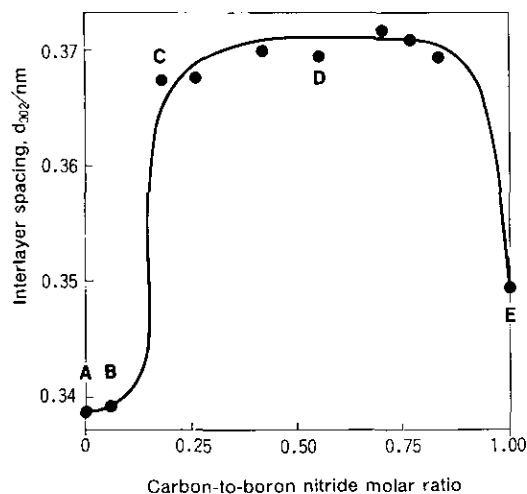
FIG. 4. Relationship between the interlayer distance d_{002} and C/BN molar ratio in B–C–N chemical mixtures prepared at 1300°C.

chanical mixtures of the two constituents obtained from the fused mixture of boric acid with urea (tBN) and saccharose with urea (tC), respectively. Series B consisted of materials prepared from a fused mixture of boric acid and urea with a varying saccharose ratio. Those powders were prepared at 1500°C. The spectra of both series are shown in Fig. 7.

The boron nitride spectrum shows two absorption peaks, around 1375 and 815 cm⁻¹, ascribed to the in-plane and out-of-plane modes, respectively. Increasing carbon content did not influence the shape of the spectra of the mechanical mixture samples (column A) as carbon is known to be inactive with infrared radiation. In the chemical mixtures (column B) the following phenomenon was observed: when the carbon content was increased, the intensity of the 815 cm⁻¹ peak diminished, and the peak was hardly observable when sample composition was near the formula BC_4N (column B, sample III).

4. DISCUSSION

The set of lines in the ternary diagram showed that the products obtained from the fused mixture of the three compounds still kept a partially organic character up to 500°C due to the presence of urea-derived remainders and to incomplete carbonization of saccharose. No substantial differences in the shape of the curves were recognized from 700°C upward. This suggests chemical simi-
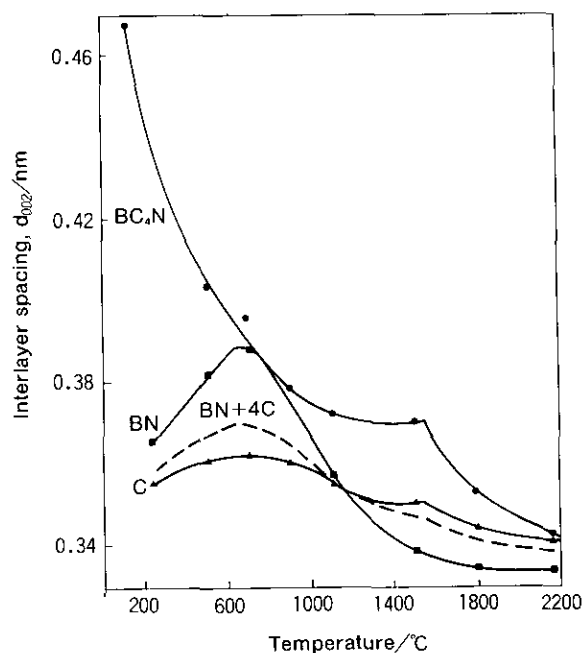
in Fig. 4. The best ordering was found in the case of a carbon-free tBN (A) and in the sample containing boron carbide (B). These samples were followed by pure carbon (E). The worst but mutually comparable ordering was observed in all the complex samples.

The annealing temperature dependence of the d_{002} parameter was measured for three samples—boron nitride, carbon, and the complex substance with a C/BN molar ratio approximately equal to 4 and is shown in Fig. 5. There is a general tendency for the interlayer distance to shorten with increasing temperature. This tendency was the most significant in the case of the complex sample, but within the examined range its interlayer distances remain the longest. In the case of the terminal substances (boron nitride and carbon, respectively), local maxima were found around 700°C. Above this temperature the tendency toward closer packing was common, and particularly the profiles for carbon and the complex samples were similar.

SEMs are shown in Fig. 6 for the powder samples prepared at 1500°C. Boron nitride (A) was a powder composed of typical tabular grains. Carbon (B) had irregular, porous grains without any geometrical distinction, reflecting the foamy character of the precursor and consecutive milling. The shape of the complex sample particles (C) was very similar to that of the carbon sample.

3.3. Infrared Spectroscopy

Infrared spectroscopy was applied to resolve the problem of whether the samples prepared via the liquid phase were real compounds or merely mixtures of carbon with boron nitride. Two series of specimens were prepared for this purpose. The specimens in series A were simple me-

FIG. 5. Annealing temperature dependencies of the interlayer distance d_{002} of carbon, boron nitride, and BC_4N powders, and BN + 4C powder mixture.
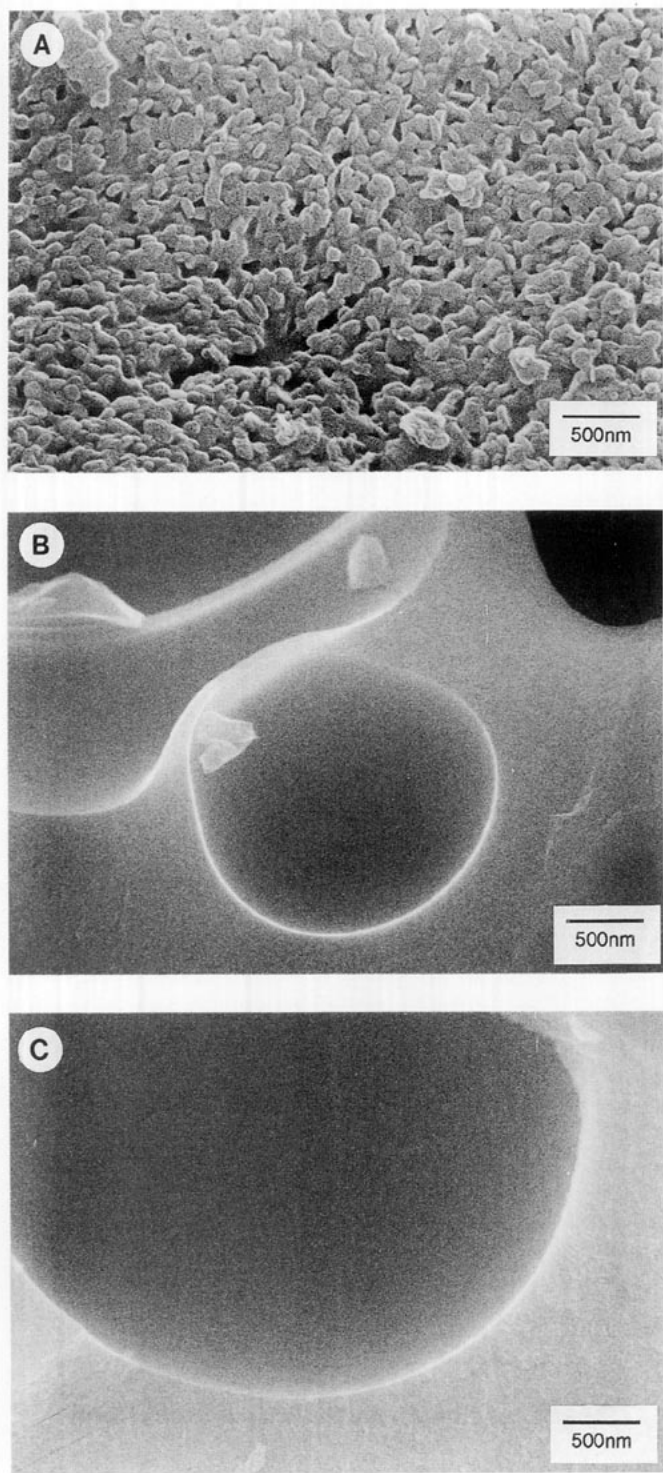
FIG. 6.   Scanning electron micrographs of boron nitride (A), carbon (B), and BC$_4$N (C) powders prepared at 1500°C.

formed from the urea–boric acid system at the same temperature when the supply of nitrogen is insufficient. Such a form of boric oxide must be much more reactive than glassy oxide for it to be converted into boron carbide by introduction of carbon from saccharose. At 1500°C the reducing effect of carbon was completed, as all the products were oxygen-free.

It can be seen from the lines in the ternary C–N–O diagram that chemical interaction between carbon and boron nitride proceeded to a certain limit recognized by inflection points in the lines. The linear shape beyond the inflection point toward the carbon vertex suggested that above the saturation limit, excessive carbon separates without any interaction with boron nitride. This saturation state nearly corresponds to the formula BC$_4$N.

Apparently, the B–C–N substance prepared by the fusion process was a layered material of highly disordered structure. Contrary to expectation, the interlayer distance of the material was not an average value of those of boron nitride and carbon but the distance was much longer than for tBN and tC within the entire range of BN/C ratio and temperature. This fact strongly suggests a chemical interaction between the constituents. The temperature dependence of the interlayer distance and a comparison with both constituents testify to a structural resemblance between carbon and a B–C–N compound. Carbon rather than boron nitride is thus considered to control the structure of the complex compound.

Other evidence of the interaction between boron nitride and carbon is provided by infrared spectroscopy. If there is no change in infrared spectra with carbon con-
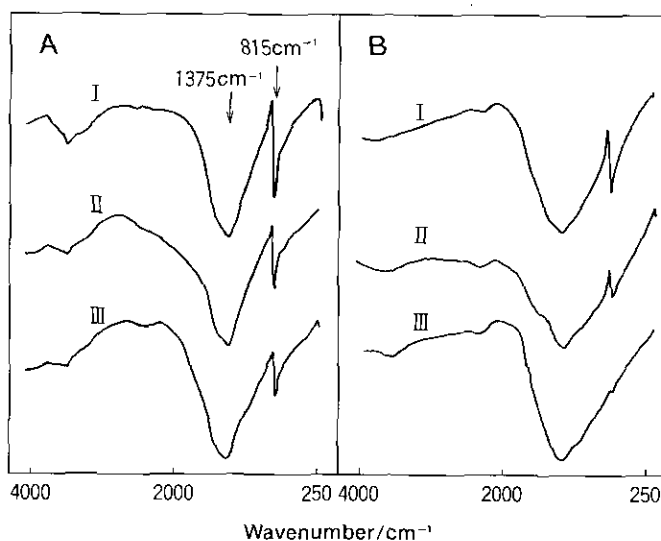
larity among the products. At 1300°C, the presence of boron carbide was revealed in samples with rather low carbon content. We have shown in a previous paper (20) that crystalline boric oxide accompanies boron nitride

FIG. 7.   Infrared spectra of mechanical (A) and chemical (B) mixtures of boron nitride and carbon with varying C/BN ratio, and BC$_x$N powders, prepared at 1500°C. (A) I, 10% C; II, 50% C; and III, 70% C; (B) I, 3.9% C; II, 32.6% C; and III, 64.28% C.

tent, formation of a ternary compound can be excluded. If these three atoms occupy the same planar macromolecules, the number of modes must increase due to additional chemical bonds such as C–N and B–C. In our experiments, increasing the carbon content in the sample led to decreasing absorption due to the out-of-plane mode of hexagonal boron nitride, which finally disappeared when the C/BN ratio was equal to 4. It is considered that carbon, which itself is inactive to infrared absorption, is blocking the out-of-plane mode of boron nitride without affecting the line due to the in-plane mode. Thus a B–C–N substance obtained via the liquid phase, possessing the balanced composition BC_4N, has a layer-based structure with abnormal interlayer expansion and completely blocks the out-of-plane infrared mode. Basically, graphite and hBN are stable phases in the B–C–N system; thus it is plausible that the hexagonal net planes of carbon and boron nitride might be formed simultaneously. Such a consideration had led us to propose the following model to explain the intralayer and interlayer characters of the B–C–N substance.

1. The proposed model is based on a turbostratic structure with the repeating sequence ... *ABAABAABA* ..., where *A* and *B* are the carbon and BN layers, respectively, as shown in Fig. 8. The enhanced turbostraticity can be explained by a difference in bond distances between C–C (0.142 nm) and B–N (0.145 nm) which results in stress during construction of a three-dimensional B–C–N structure. The discrepancy prohibits building up a regular crystal lattice; the crystallinity is even poorer than those of isolated constituents, and the following sequence occurs within the entire investigated temperature range and at any C/BN ratio:

$$d_{002} (BC_xN) > d_{002} (tC) > d_{002} (tBN). \qquad [1]$$

The disappearance of the out-of-plane infrared active mode is a consequence of the enclosure of each BN layer in the structure by a pair of carbon layers.

2. Simultaneous formation of the two-dimensional nuclei of both boron nitride and carbon in the precursor is the first step in B–C–N formation. The different chemical natures of these two types of layers and the coexistence of volatile residue due to the chosen low temperature for precursor preparation give rise to an extreme expansion of the interlayer distance compared with those of tBN and tC precursors.

By further heating in order to release residual ligands, the nuclei grow, and at the balance composition, triple layers are obtained, which are the structural units of the BC_4N solid:

$$C_{2n} + (BN)_n + C_{2n} = (BC_4N)_n. \qquad [2]$$
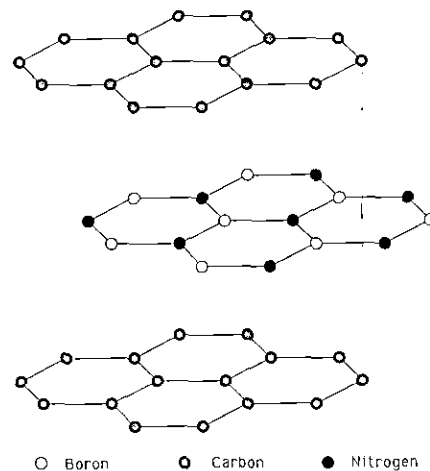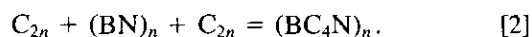

O Boron   O Carbon   ● Nitrogen

FIG. 8. Proposed scheme of boron nitride and carbon layers in a BC_4N compound.

The pyrolysis of gases is a very rapid process compared with that of the condensed system. The B, C, N elements coexist in a variety of combinations reflecting chemical character and random arrangement of gaseous precursors. In the structural model after Kaner *et al.* [6], a coexistence of all three elements can thus be supposed. Due to chemical bond stress within the layers, such a compound has relatively low stability. A rearrangement of the three elements to form a more stable lattice is rather difficult and therefore only decomposition to graphite and boron carbide was observed after additional heating above the temperature of pyrolysis (3, 12).

We suppose in our model that separate formation of carbon and boron nitride nuclei is the first step. These planar nuclei are generated from a liquid phase which plays three roles—it stabilizes the nuclei by interaction with peripheral nodes, ensures their mobility, and supports them with additional material to proceed their growth, as was already suggested for tBN formation from the fused urea–boric acid mixture (21). When the carbon and boron nitride monolayers reach a certain size, mutual attraction of van der Waals type makes it possible to build "carbon–boron nitride–carbon" triple layers, which then form a layered solid with significant interlayer expansion. The turbostraticity comes from misfitting of (*hk*0) lattice constants between hBN and graphite. On the other hand, such an arrangement is stable, as heating at 2150°C did not result either in recrystallization or in disproportionation to hBN and graphite or decomposition into boron carbide. This model, based on results of chemical, XRD, and infrared analyses, is one possible candidate. Additional spectroscopic work must be carried out to support this structural idea.

5. SUMMARY

A chemical method of preparing B–C–N ternary substances have been developed. Given the character of the starting materials and the state of agglomeration of the reaction mixture based on chemical, structural, and infrared analyses, a process of a B–C–N substance and its structure have been proposed. Two-dimensional macromolecules of carbon and boron nitride are grown from a liquid phase and then linked to build a "costacked" compound with the sequence ... $C_{2n}(BN)_nC_{2n}C_{2n}(BN)_nC_{2n}$ .... A certain difference between B–N and C–C bonding lengths results in a turbostratic character and an expansion of the interlayer distance for stable graphite-like substances.

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